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HIGH TEMPERATURE APPLICATIONS OF STRUCTURAL CERAMICS

QUARTERLY PROGRESS REPORT

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INTRODUCTION

The achievement of higher efficiency thermochemical engines and heat recovery systems requires the availability of high temperature, high performance structural materials. Structural ceramics such as SiC, Si_3N_4 and certain Al_2O_3-Si_3N_4 combinations have received particular attention for these applications due to their basic characteristics of good strengths coupled with good corrosion and thermal shock resistances. Even with these positive attributes, improved reliabilities and extended lifetimes under service conditions are necessary for structural ceramics to gain industrial acceptance and use. The problems are mechanical and/or chemical in nature and are enhanced by the fact that these materials are subjected to high temperatures, reactive environments and extreme thermal gradients.

With an objective of improved performance for heat engine/heat recovery applications the NBS program on structural ceramics addresses these problems through the determination of the critical factors which influence mechanical and microstructural behavior. The activities of the program are grouped under four major subtasks with each designed to develop key data, associated test methods and companion predictive models. The status of the subtasks are detailed in the following sections.

NBS-5.12(A) - HIGH TEMPERATURE FRACTURE OF STRUCTURAL CERAMICS

DISCUSSION OF CURRENT ACTIVITIES

Silicon carbide specimens (α-SiC and KT-SiC) were fractured in the temperature range 1200 °C to 1600 °C. The through-notched specimens of α-SiC and KT-SiC showed no signs of stable crack growth prior to fracture. The K_{IC} for these through-notched specimens is higher than for a sharply cracked specimen because of the bluntness of the notch ($\rho \tilde{\approx} 250$ μm). To avoid ambiguities in the K_{IC} determined by fracture from blunt notches, chevron-notched specimens (see Figure 1) were also tested. This type of specimen tends to form a sharp crack while loading. Fracture then occurs from this sharp crack. However, analysis of K_{IC} from this type of specimen is computationally more difficult and we are at present evaluating the data. Chevron-notched specimens of KT-SiC usually showed evidence of creep crack growth prior to rapid fracture, but α-SiC samples did not.

The toughness of NCX-34 at room temperature (R.T.) was also determined this quarter using the indentation technique. This may be compared in Table 1 with the R.T. toughness determined using single-edge notched bend bars. Precracking of these bars was accomplished at 1400 °C by slow bending. The values of K_{IC} obtained by bending are significantly higher than those obtained by the indentation technique. The discrepancy is probably due to the fact that cracks introduced at elevated temperatures (i.e. creep cracks) are not nearly as sharp as those produced by indentation at R.T.

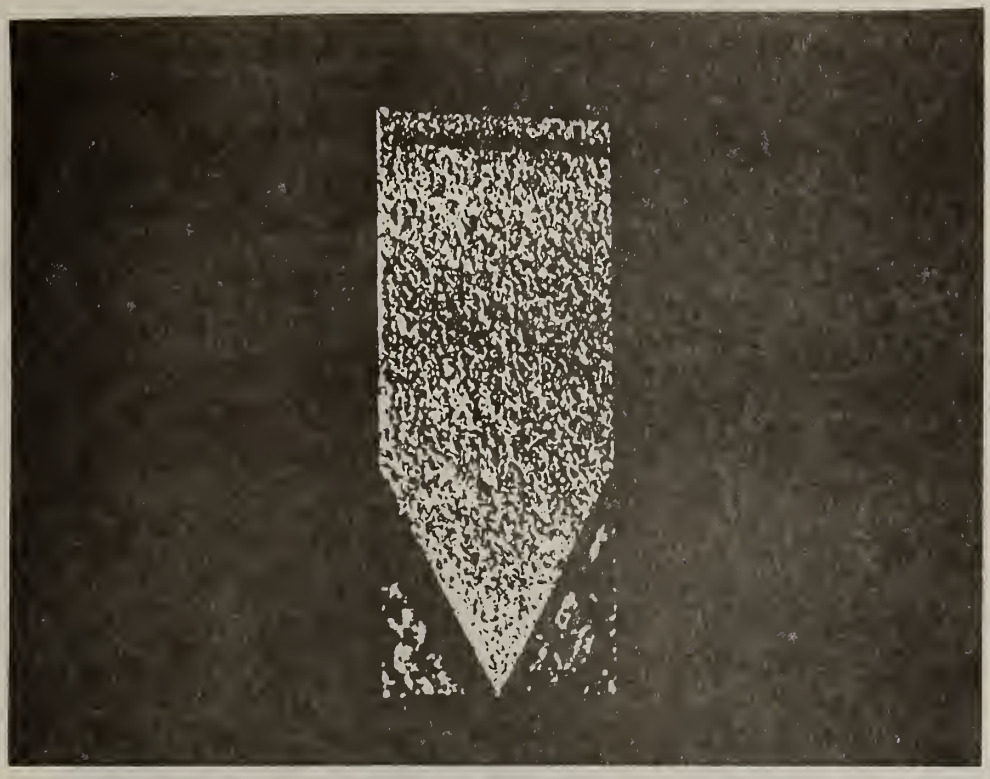

Figure 1. Broken chevron-notched bend bar of SiC showing shape of chevron.

Table 1. Fracture Data of Various Structural Ceramics

Material	Specimen Type	Temperature	K_{IC} (MPa$\sqrt{m}$	Evidence of Slow Crack Growth
α-SiC	thru-notched	1500 °C	4.06	No
α-SiC	chevron	1500 °C	9.3*	No
α-SiC	chevron	1600 °C	10.9*	No
KT-SiC	chevron	1050 °C	12.1*	---
KT-SiC	chevron	1200 °C	24.4*	Yes
KT-SiC	chevron	1350 °C	23.6*	---
KT-SiC	chevron	1400 °C	15.8*	Yes
NCX-34	indentation	R.T.	6.0	---
NCX-34	thru-notched	R.T.	9.0	---

*This data is preliminary.

NBS-5.12(B) - CRACK GROWTH MECHANISM MAPS

DISCUSSION OF CURRENT ACTIVITIES

As noted in part A above, no stable crack growth was observed in α-SiC. Notched specimens which had been held under load at 1500 °C for different lengths of time are now being examined microscopically. As shown in Figure 2 and 3, the areas near the notch were heavily cavitated. This suggests that the mechanism of failure is generalized degradation by creep cavitation as opposed to creep crack growth. We have obtained self-diffusivity data for SiC from the Diffusion Data Center at NBS in order to investigate the above contention.

Most of the data for the crack growth mechanism map of NCX-34 has been digitized and will be used to construct such a map in the immediate future.

Figure 2. α-SiC notched specimen held under 40 kg load for 26 hours at 1500 °C and then fractured. Notch root is visible at bottom of micrograph. Cavities in the material are visible in adjacent areas. (300X)

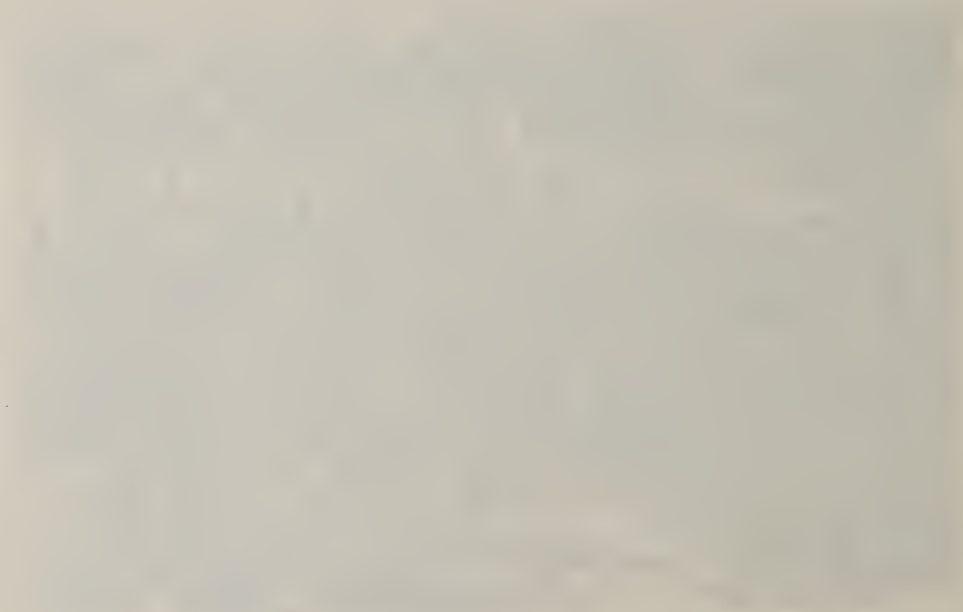

Figure 3. 5000X magnification of cavities seen in Figure 2.

NBS-5.12(C) - MICROSTRUCTURE AND PHASE ALTERATION

DISCUSSION OF CURRENT ACTIVITIES

Oxidation studies were carried out on NC203 and NC430 SiC for times up to eight hours in air. Initial oxidation proceeded rapidly in the case of siliconized SiC (NC430). This SiC continued to exude silicon with each heat treatment. The primary oxidation products formed on this material appeared to be cristobalite plus some tridymite. After a total of eight hours of oxidation at 1400 °C in air, the hot-pressed SiC (NC203) showed the first evidence of oxide layer formation. The x-ray diffraction peak obtained was tentatively assigned to cristobalite.

Work continued on the construction of a furnace for high temperature x-ray diffraction studies. Bonded ceramic fiber components and materials were received, and pieces for the furnace chamber walls are being cut and fashioned to the required shapes. Tests of the furnace are expected to begin in April.

Two approaches are under investigation for the fabrication of the heating element. The first approach is the utilization of the sample as the heating element. Since the SiC samples generally have very high resistances, it is necessary to apply a stable conductive coating to the underside of the samples. Since we were informed that a stable plasma-sprayed coating was difficult to achieve on SiC, we undertook the investigation of several fired-on compositions consisting of silicon carbide, silicon, carbon, dopants, and binders. Although it has been possible to form "hard" coatings, a low-resistance coating has not been achieved to date.

As a second approach, heating elements have been machined from the central portion of SiC heating elements. Although this approach appears to be feasible, present constraints on the design may introduce too high a limit on (2θ)-range at low (2θ) angles. Also, the larger thermal mass introduced into the furnace is undesirable. Nevertheless, this approach is being pursued to put the furnace into operation and to gain some experience with it.

Activities are also continuing to develop a model for induced microstresses and microstrains. Since bulk materials generally contain cracks and inclusions without well characterized regularities, mathematical idealizations generally involve special circumstances which permit their solution. Presently, an attempt is being made to strike a balance between what is desirable physically and what is tractable theoretically. Idealizations are being sought which will render the problem of a simultaneous array of cracks and inclusions tractable. It is hoped that such a model will retain the essence of the physical situation for a broad class of materials while possessing symmetries useful for a mathematical solution.

Some primary difficulties we have encountered in the development of the model are as follows. Complex stress functions and conformal mapping techniques have been applied successfully to isolated extended inclusions in a contiguous infinite medium. An inclusion has a well defined bounding surface within which the material properties are continuous and

uniform. Cracks, on the other hand, have regions of plasticity at the crack ends, and the mathematical difficulties associated with this feature have caused an alternative to the conformal mapping techniques to be sought. This has led to an idealization in which a crack is treated as a slit which mathematically becomes a straight line cut in a plane. Such a cut is formally a displacement discontinuity. But, edge and screw dislocations are also displacement discontinuities. Consequently, it is possible to find a distribution of these dislocations to represent a slit-like crack. The advantage of this is that the strain state for an edge or screw dislocation is known; and, hence, the strain state for the crack can be computed from the equivalent distribution of dislocations. The problem with this approach is that it works only for simple displacement discontinuities; which, therefore, excludes extended inclusions. Consequently, a mixed problem of cracks and inclusions probably will have to be developed in the complex potential formalism.

Two considerations which must yet be given attention are the applicability of numerical solution techniques for the mixed problem and the possibility of using rather general Green's function formulations.

NBS-5.12(D) - MICROSTRUCTURE AND FRACTURE IN REACTIVE ENVIRONMENTS

DISCUSSION OF CURRENT ACTIVITIES

The construction of an apparatus for fracture mechanical testing of selected structural ceramics in controlled gaseous environments at high temperature is almost completed. An existing gear-driven loading machine was readied for use, its worn out gear drive having been replaced. This machine can produce a displacement rate as low as 0.5 μm/min for crack propagation studies. A commercially manufactured gas-tight box furnace (15 cm cube hot zone) was delivered the first week of February. Molybdenum disilicide heating elements were installed in the furnace, and the furnace was wired to an automatically controlled power supply. The furnace was established level in the frame of the loading machine, and silicon carbide loading rods were appropriately secured in special bellows assemblies attached to the top and bottom ports of the furnace. A thermostated bath was set up to generate a given partial pressure of

water vapor which will be combined with a gas flow through the furnace. The bath will be used to control the water vapor generator and the cooling of the furnace shell and bellows assemblies to prevent water condensation in the furnace. Supplies of oxygen, nitrogen, carbon dioxide, and sulfur dioxide gases along with their flow controllers are available. Their connections to the furnace and to an established exhaust system will complete the assembly of the apparatus.

Double torsion specimens and chevron notched, four point bending specimens are being prepared for crack propagation and fracture toughness studies, respectively. Both sintered alpha silicon carbide and siliconized (KT) silicon carbide billets were obtained commercially and are being diamond sawed to make the specimens. The fracture mechanical tests will commence in the immediate future.

A second furnace and attendant gas lines were assembled for reaction studies between SiC and gases other than oxygen which are components of flue gases from coal-fired power plants. These gases include SO_2, CO_2, CO, N_2, and water vapor. Since N_2 is expected to be relatively non-reactive at oxygen activities contemplated in this study, it will be used primarily as a carrier or dilutant gas for this study. Sulfur dioxide (1000 ppm in N_2) is the first gas selected for study. It will be used dried and containing controlled amounts of water vapor. We are awaiting delivery of a SO_2-N_2 mixture.